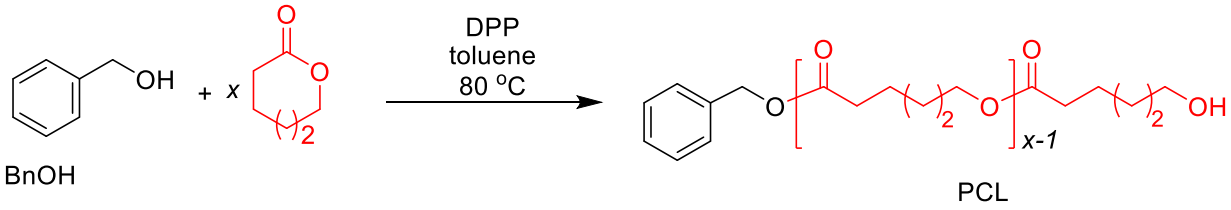
Supporting information

Block Copolymers of Macro/Small Lactones by a "Catalyst-Switch" Organocatalytic Strategy. Thermal Properties and Phase Behaviour

Viko Ladelta,[a] Joey D. Kim,[a,#] Panayiotis Bilalis,[a] Yves Gnanou,[b] Nikos Hadjichristidis[a]*

King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia.
[a]Physical Sciences and Engineering Division, KAUST Catalysis Center, Polymer Synthesis Laboratory
[b]Physical Sciences and Engineering Division
[#]Permanent address:Department of Chemical Engineering, CALTECH, Pasadena, 91125, USA
E-mail: nikolaos.hadjichristidis@kaust.edu.sa



Scheme S1. ROP of CL catalyzed by DPP ($[CL]_0$ = 1 M, $[OH]_0$:$[DPP]_0$ = 1:2, 80 °C).

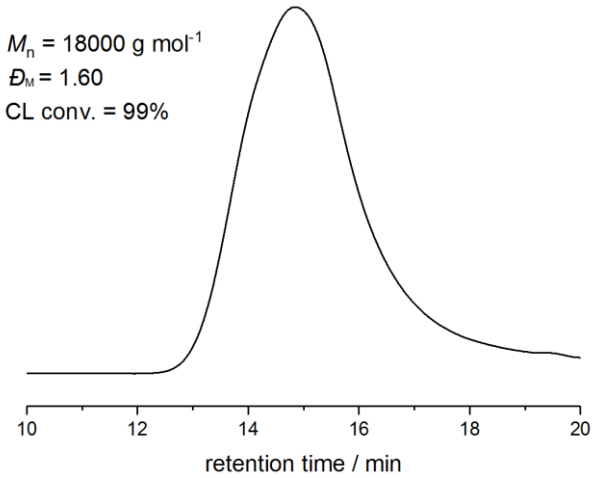


Figure S1. GPC trace of PCL prepared by ROP with DPP as catalyst (THF, 35 °C, PS standards).

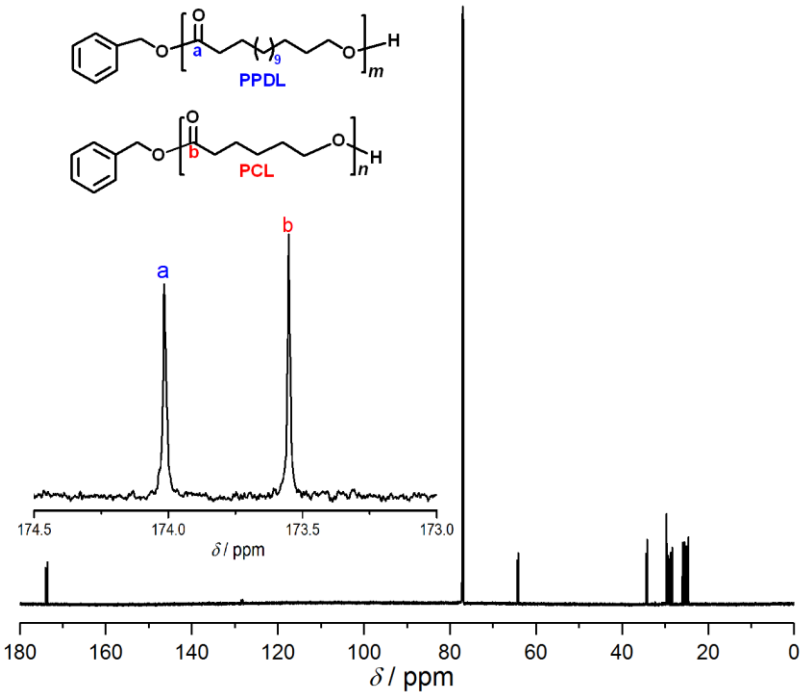


Figure S2. 239 MHz ^{13}C NMR spectrum of PPDL:PCL mixture in $CDCl_3$ at room temperature (rt).

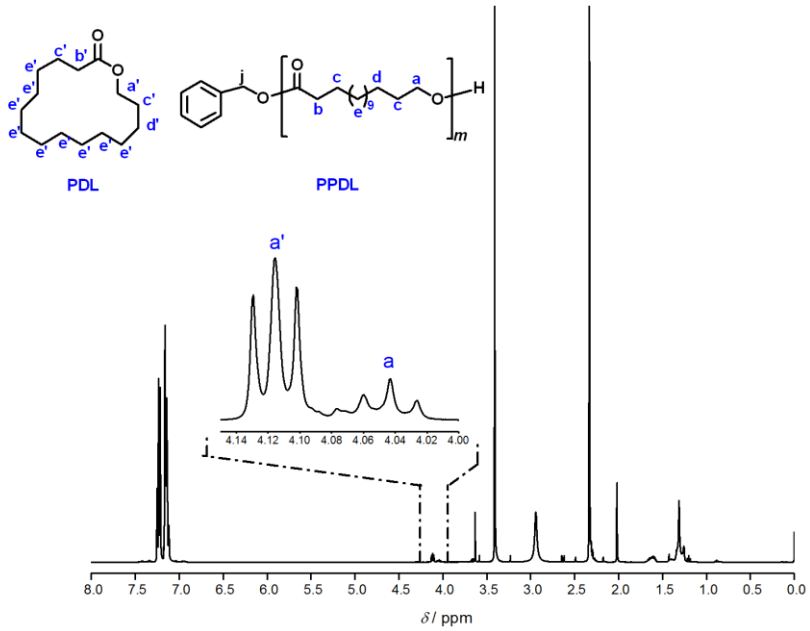


Figure S3. Determination of PDL conversion to PPDL from ^{1}H NMR spectrum of reaction mixture after 10 min by 500 MHz spectrometer ($CDCl_3$, rt).

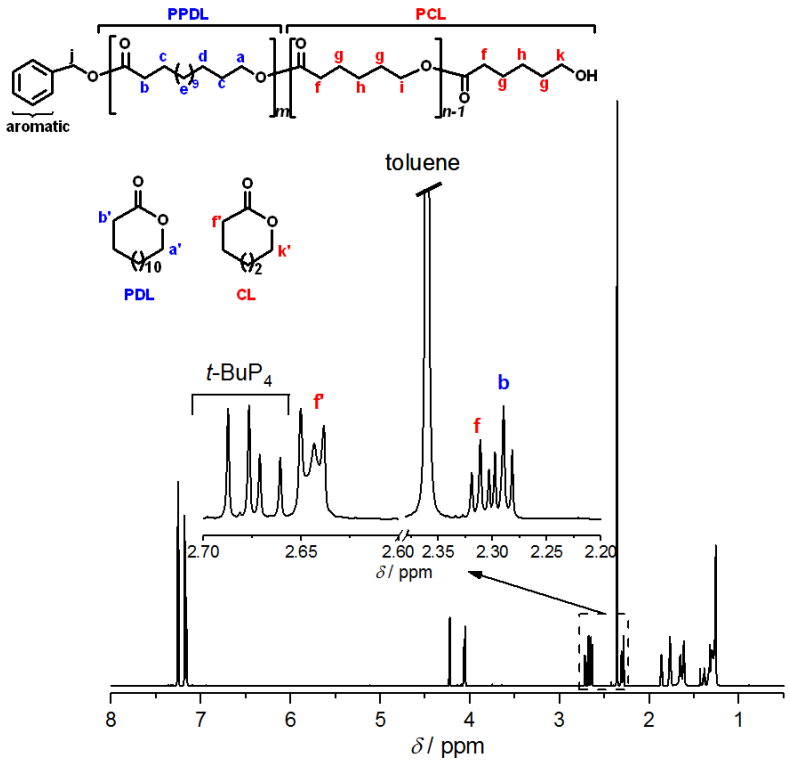


Figure S4. Determination of PCL conversion during the catalyst-switch synthesis of PPDL-*b*-PCL from ^{1}H NMR spectrum of reaction mixture after 6 h by 950 MHz ($CDCl_3$, rt).

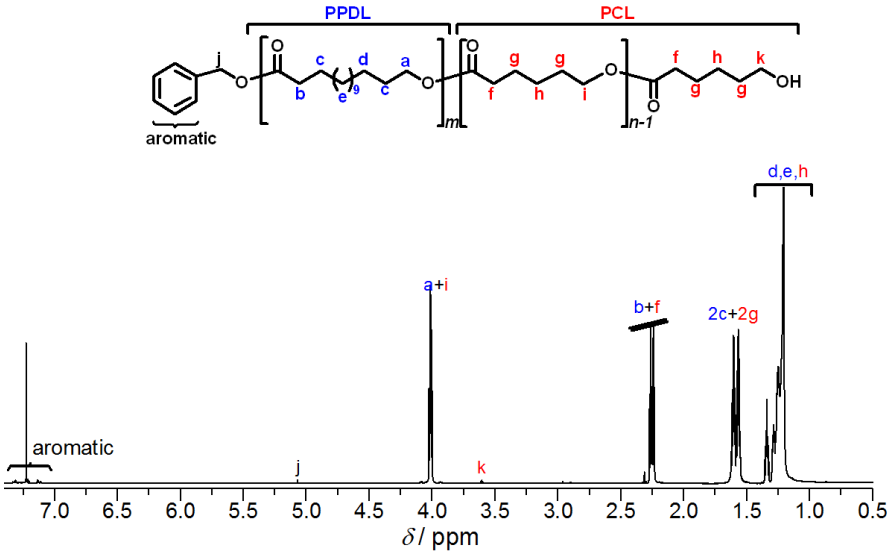


Figure S5. 950 MHz ^{1}H NMR spectrum of PPDL-*b*-PCL (entry 1, Table 2) prepared by catalyst-switch strategy ($CDCl_3$, rt).

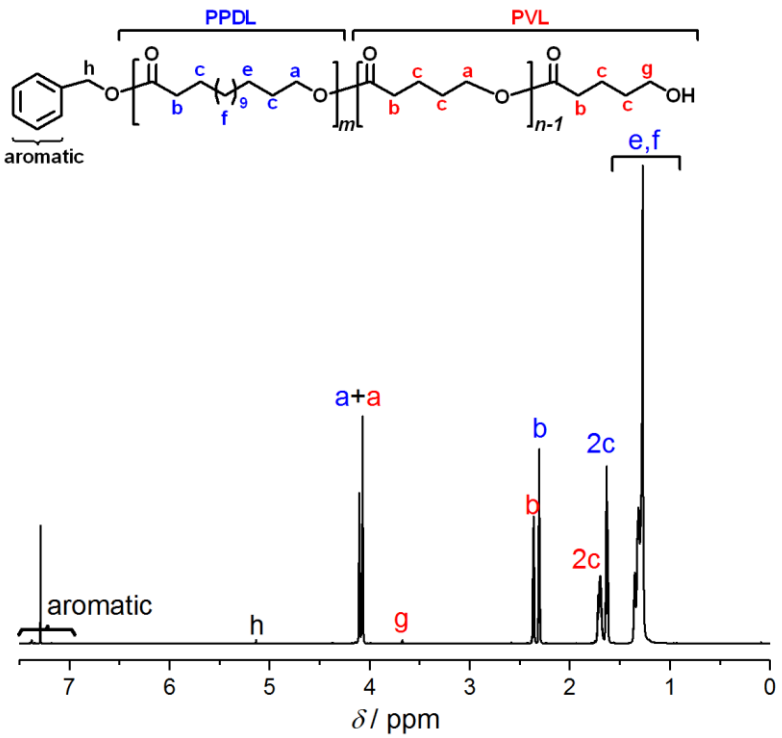


Figure S6. 950 MHz ^{1}H NMR spectrum of PPDL-*b*-PVL (entry 2, Table 2) prepared by catalyst-switch strategy ($CDCl_3$, rt).

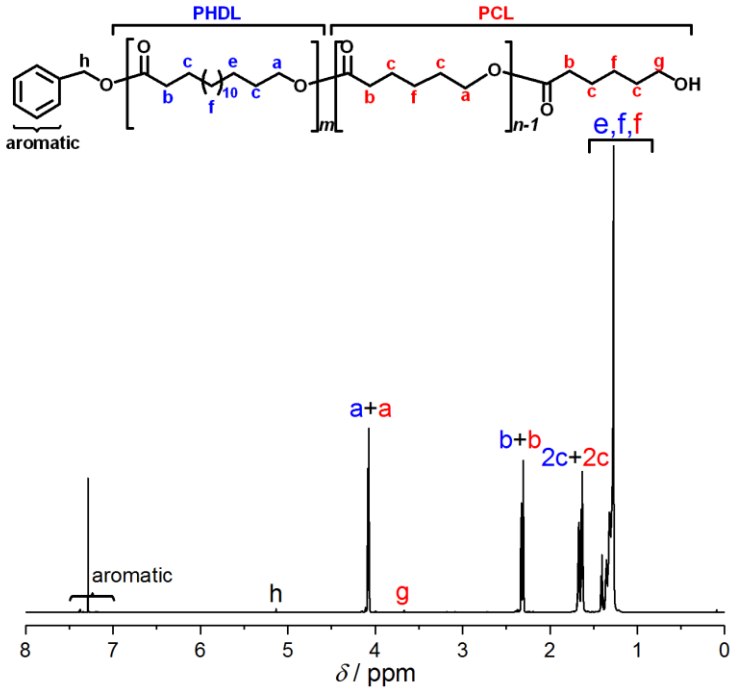


Figure S7. 950 MHz ^{1}H NMR spectrum of PHDL-*b*-PCL (entry 3, Table 2) prepared by catalyst-switch strategy ($CDCl_3$, rt).

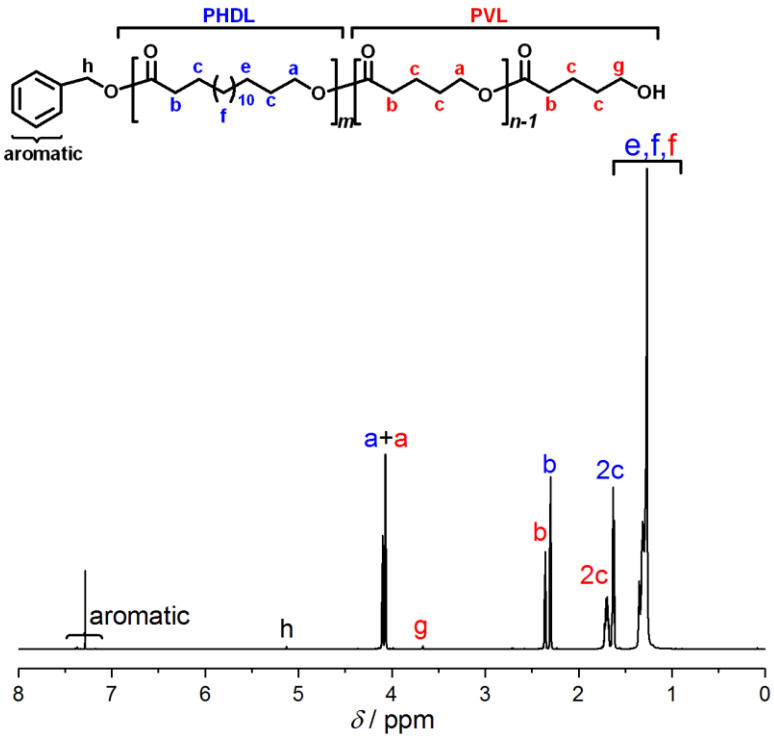


Figure S8. 950 MHz ^{1}H NMR spectrum of PHDL-*b*-PVL (entry 4, Table 2) prepared by catalyst-switch strategy ($CDCl_3$, rt).

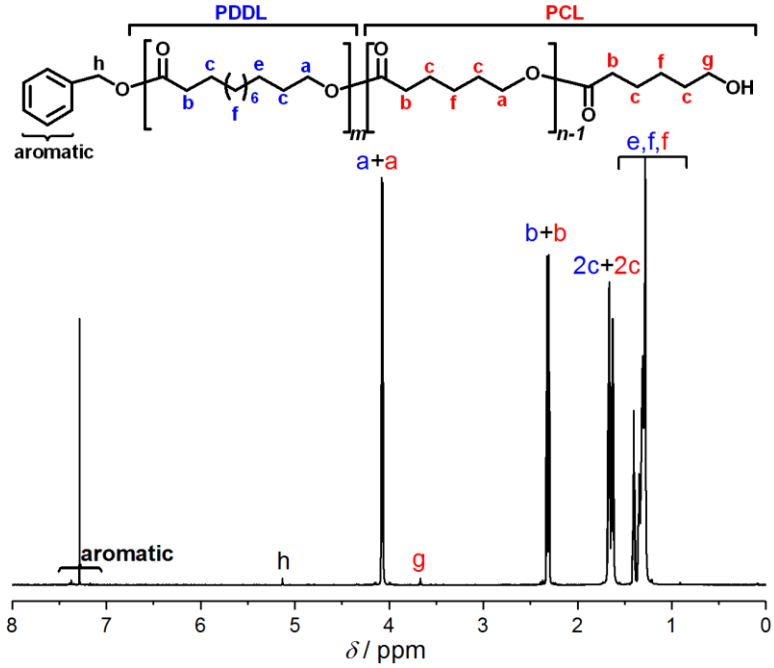


Figure S9. 950 MHz ^{1}H NMR spectrum of PDDL-*b*-PCL (entry 5, Table 2) prepared by catalyst-switch strategy ($CDCl_3$, rt).

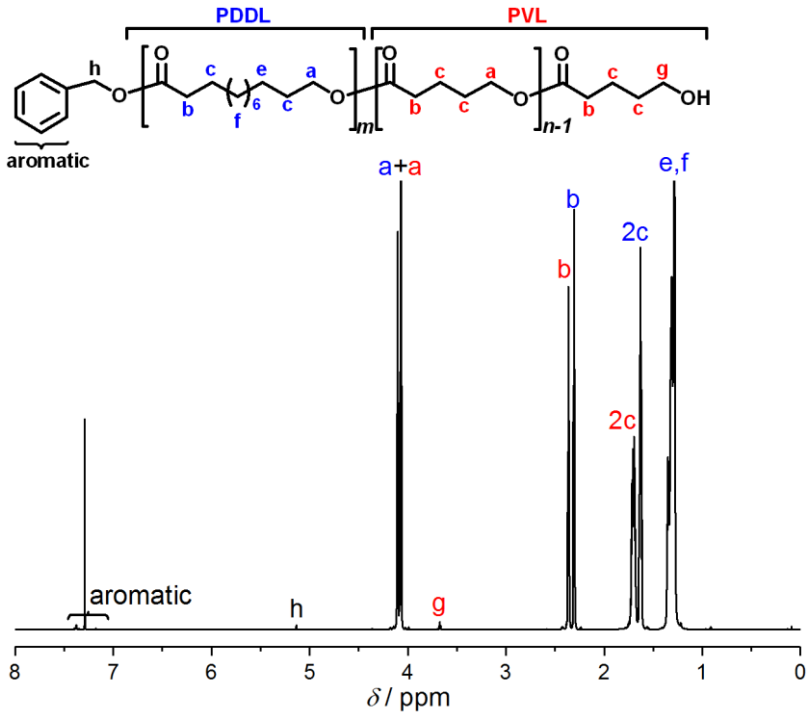


Figure S10 950 MHz ^{1}H NMR spectrum of PDDL-*b*-PVL (entry 6, Table 2) prepared by catalyst-switch strategy ($CDCl_3$, rt).

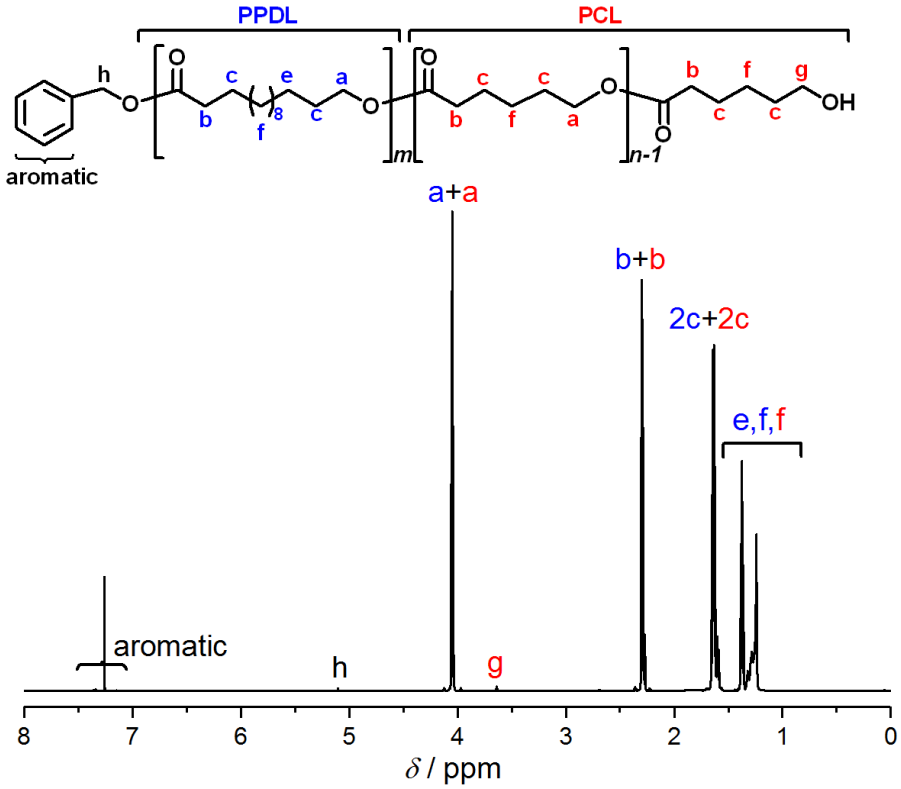


Figure S11. 950 MHz ^{1}H NMR spectrum of $PPDL_{50}$-*b*-PCL_{400} (entry 7, Tale 2) prepared by catalyst-switch strategy ($CDCl_3$, rt)

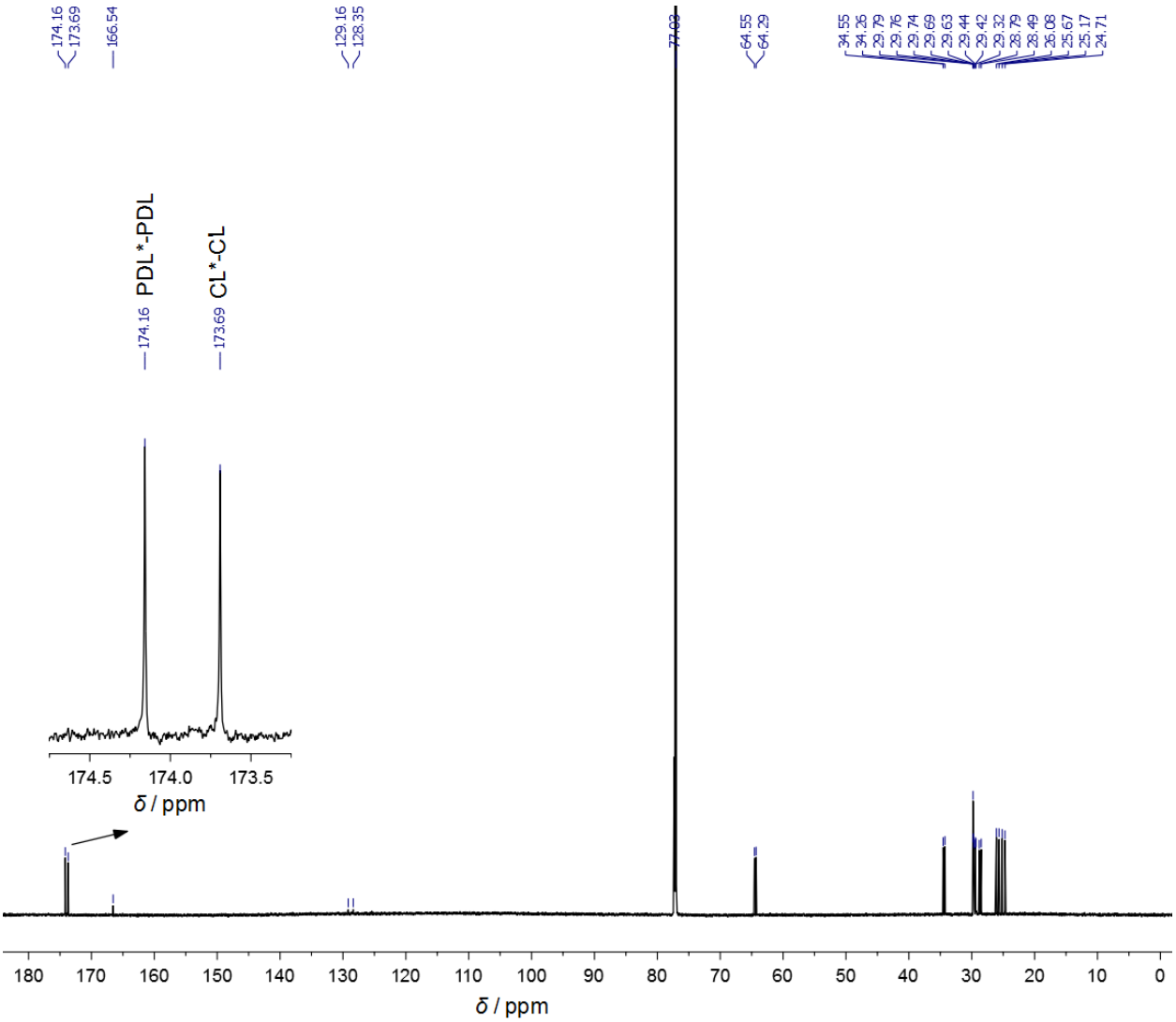


Figure S12. 239 MHz ^{13}C NMR spectrum of PPDL-*b*-PCL (entry 1, Table 2) prepared by catalyst-switch strategy ($CDCl_3$, rt).

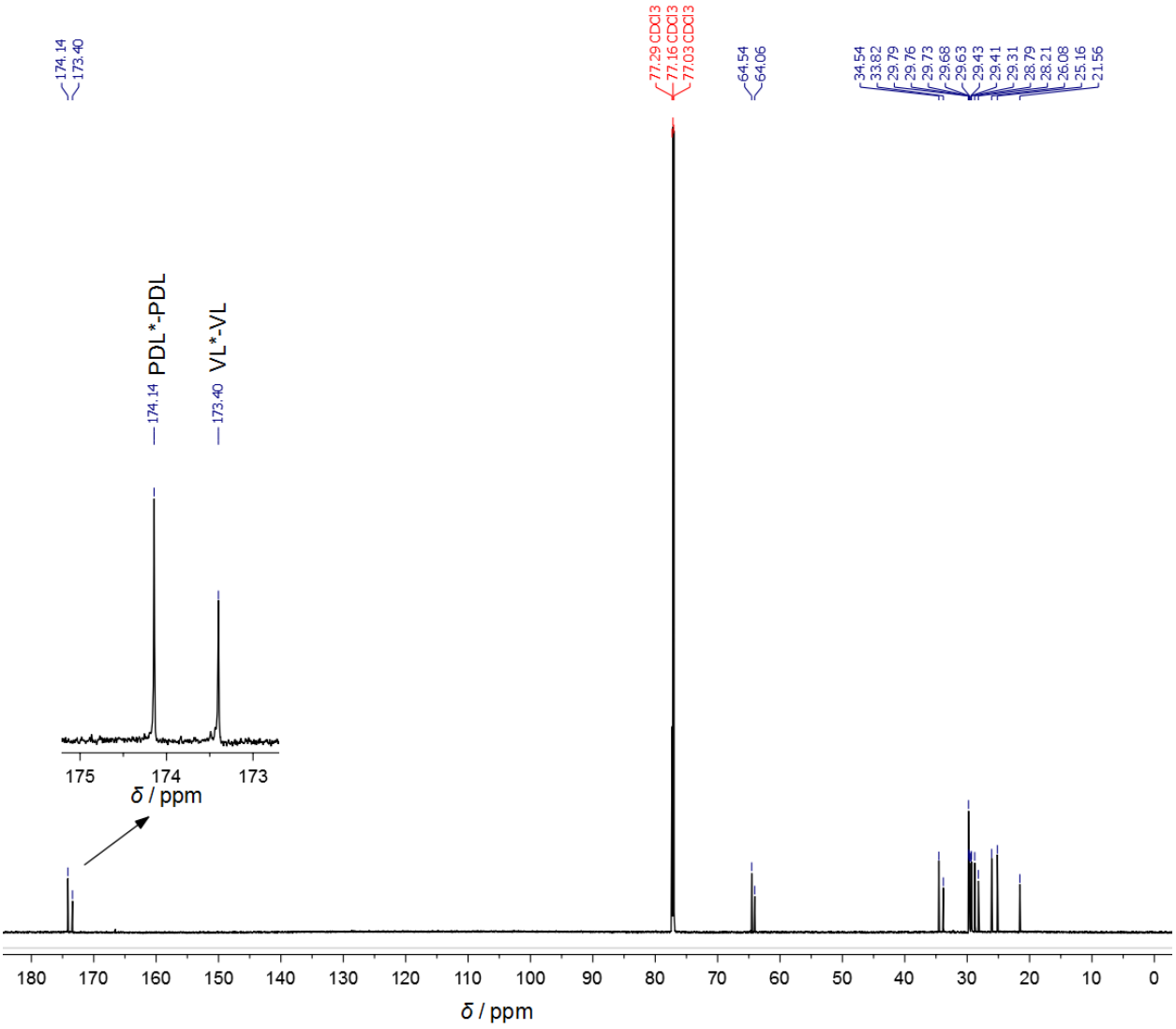


Figure S13. 239 MHz ^{13}C NMR spectrum of PPDL-*b*-PVL (entry 2, Table 2) prepared by catalyst-switch strategy ($CDCl_3$, rt).

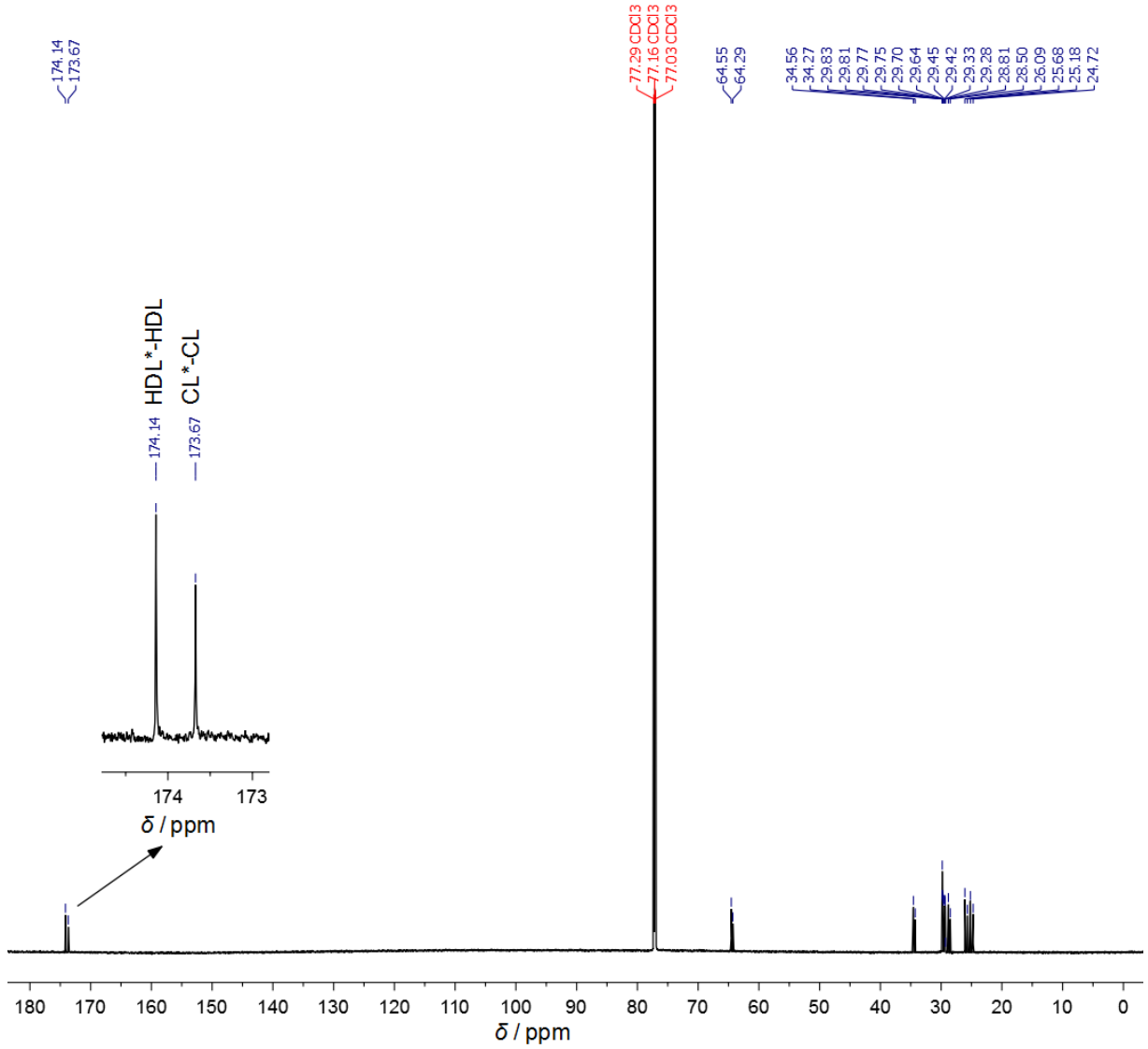


Figure S14. 239 MHz ^{13}C NMR spectrum of PHDL-*b*-PCL (entry 3, Table 2) prepared by catalyst-switch strategy ($CDCl_3$, rt)

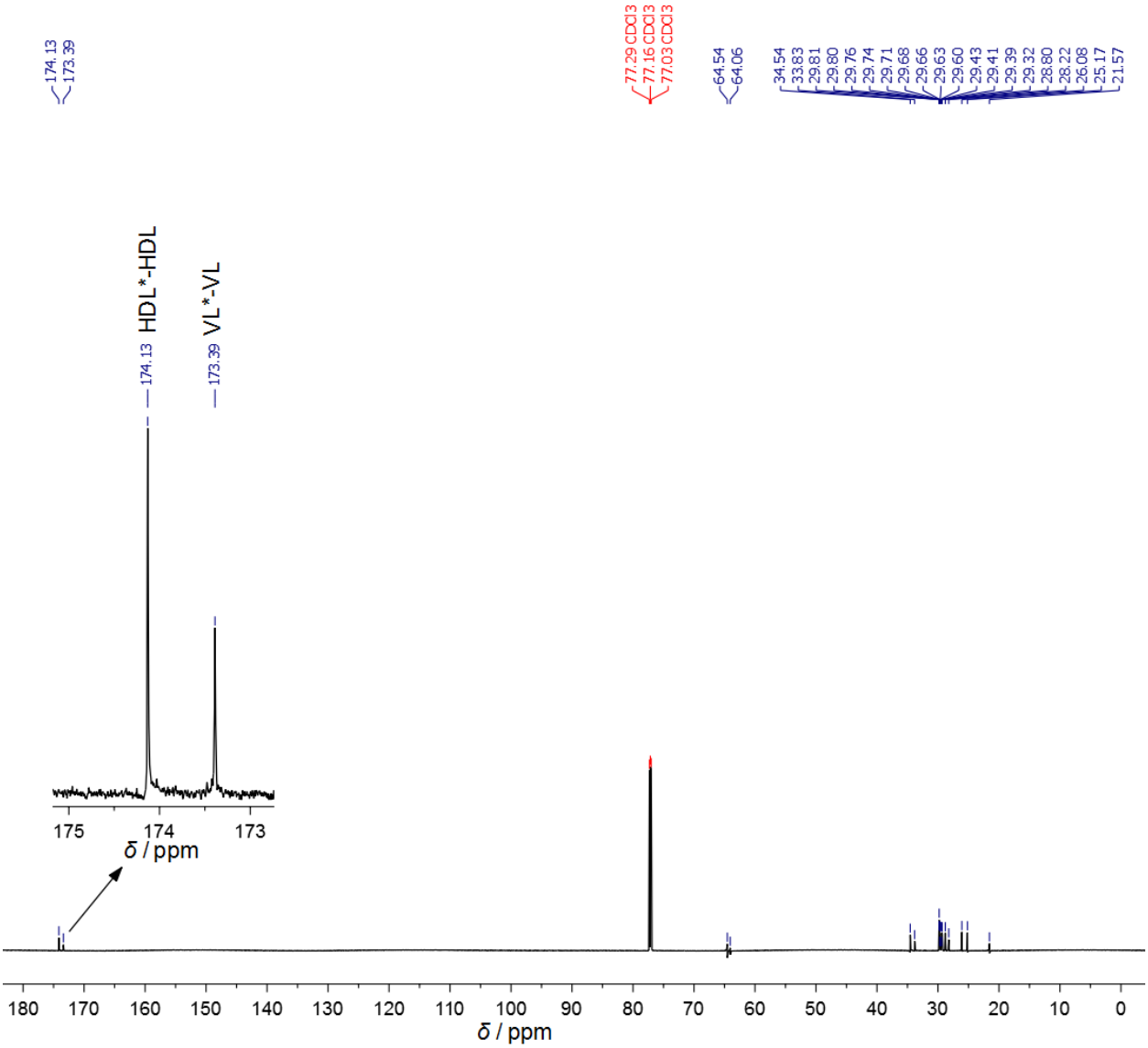


Figure S15. 239 MHz ^{13}C NMR spectrum of PHDL-*b*-PVL (entry 4, Table 2) prepared by catalyst-switch strategy ($CDCl_3$, rt)

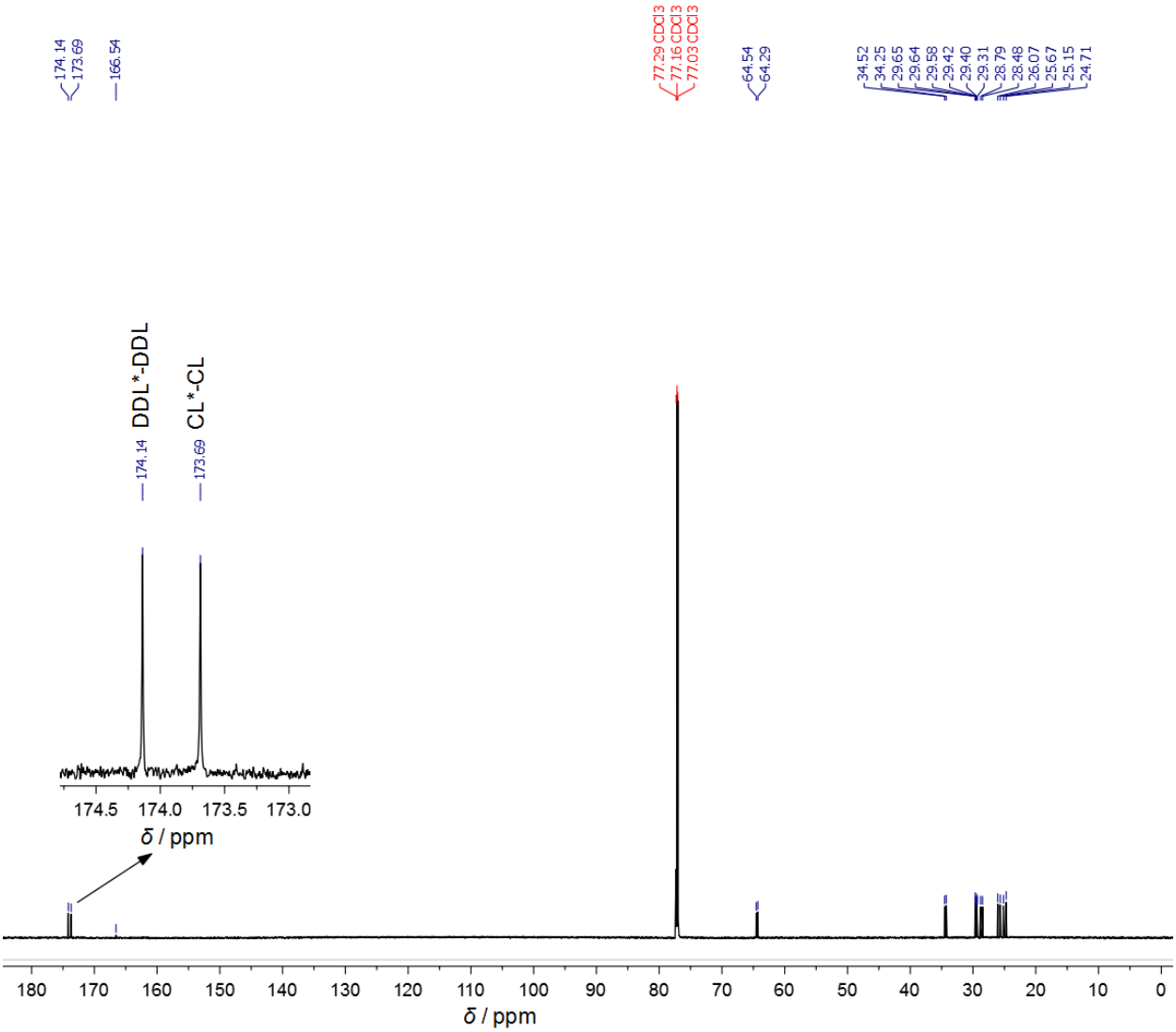


Figure S16. 239 MHz ^{13}C NMR spectrum of PDDL-*b*-PCL (entry 5, Table 2) prepared by catalyst-switch strategy ($CDCl_3$, rt)

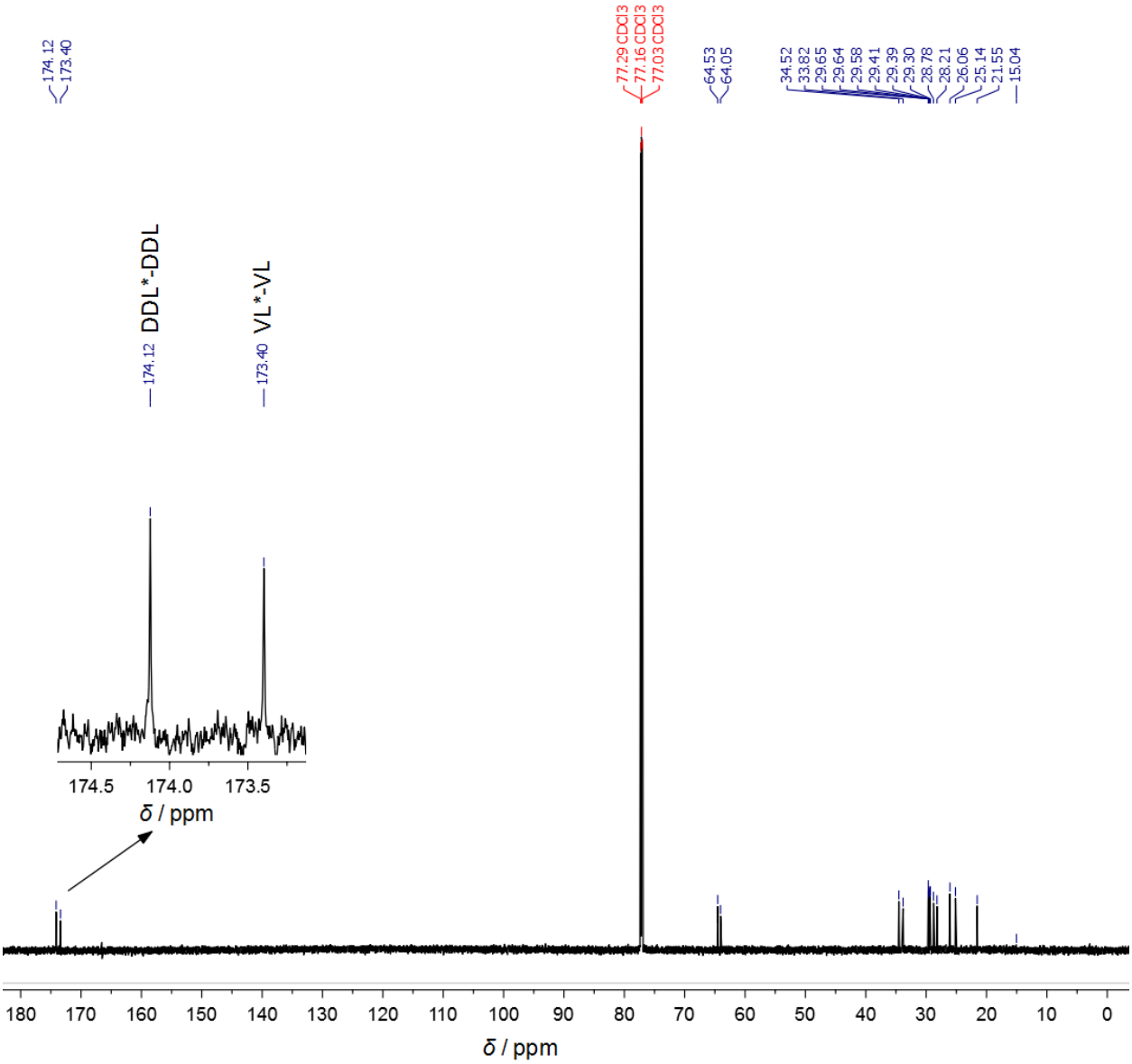


Figure S17. 239 MHz ^{13}C NMR spectrum of PDDL-*b*-PVL (entry 6, Table 2) prepared by catalyst-switch strategy ($CDCl_3$, rt)

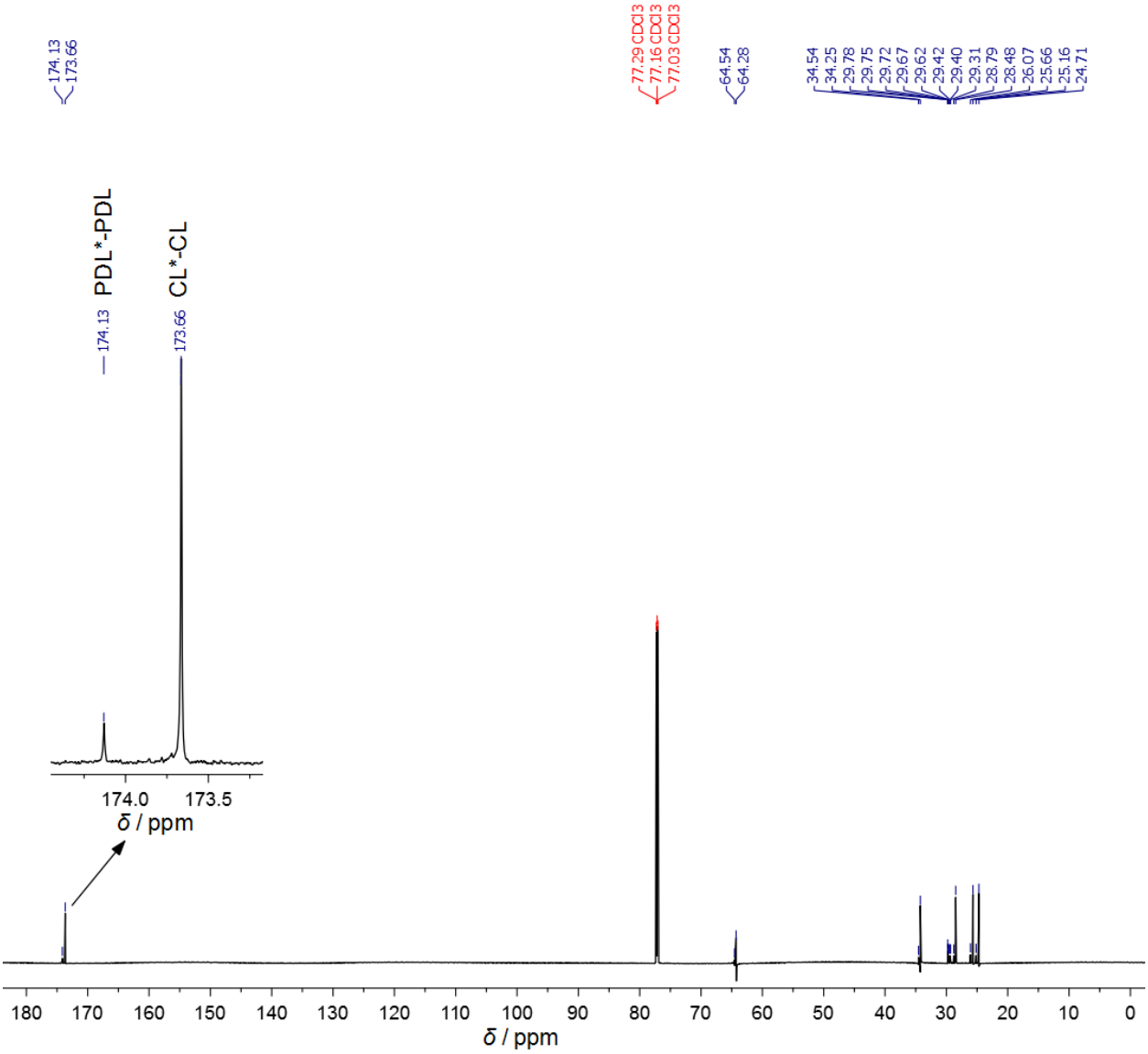


Figure S18. 239 MHz ^{13}C NMR spectrum of $PPDL_{50}$-*b*-PCL_{400} (entry 7, Table 2) prepared by catalyst-switch strategy ($CDCl_3$, rt)

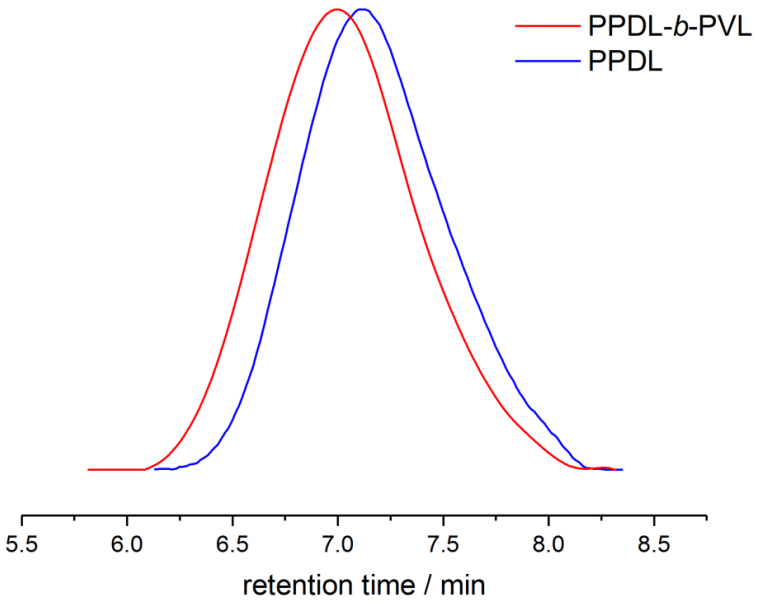


Figure S19. HT-GPC traces of PPDL (blue) macroinitiator and PPDL-*b*-PVL (red, entry 2, Table 2) prepared by catalyst-switch strategy (TCB, 150 °C, PS standards).

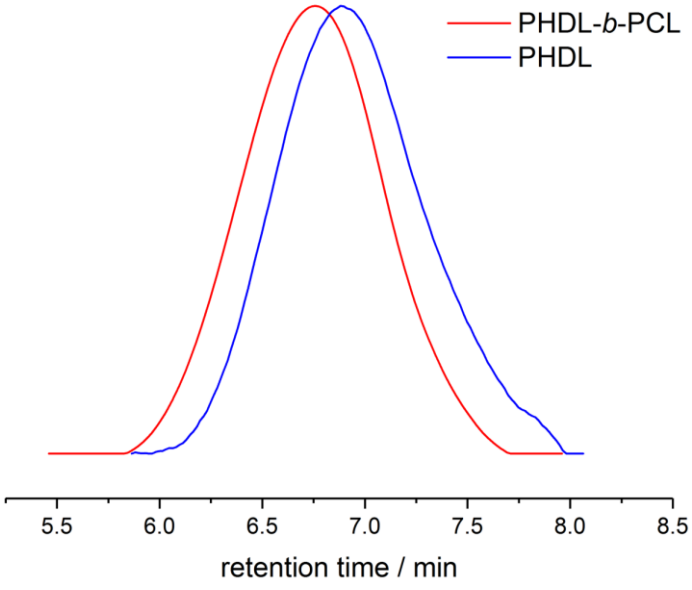


Figure S20. HT-GPC traces of PHDL (blue) macroinitiator and PHDL-*b*-PCL (red, entry 3, Table 2) prepared by catalyst switch-strategy (TCB, 150 °C, PS standards).

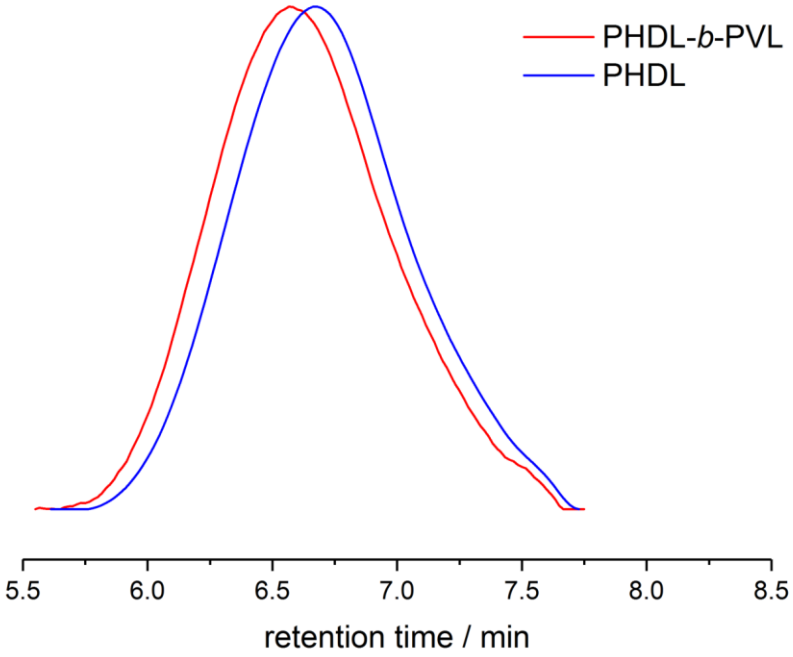


Figure S21. HT-GPC traces of PHDL (blue) macroinitiator and PHDL-*b*-PVL (red, entry 4, Table 2) prepared by catalyst switch-strategy (TCB, 150 °C, PS standards).

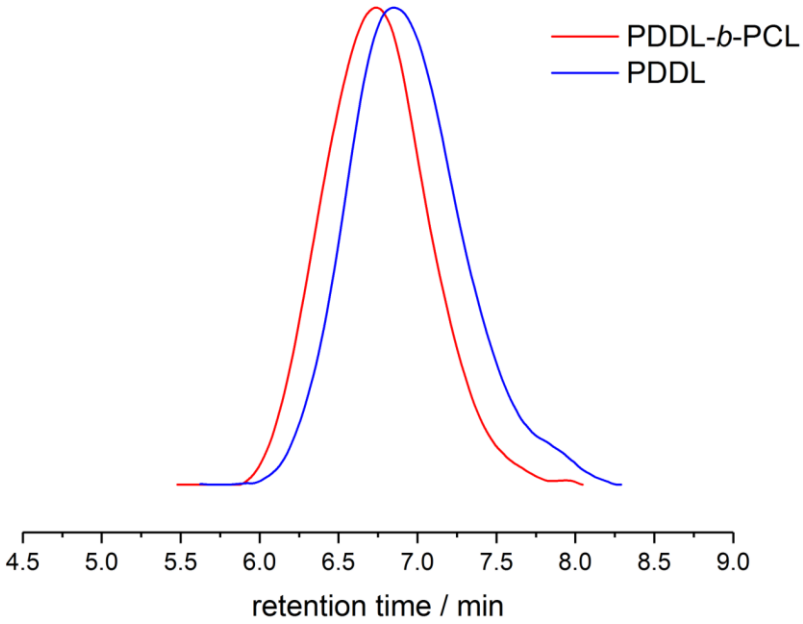


Figure S22. HT-GPC traces of PDDL (blue) macroinitiator and PDDL-*b*-PCL (red, entry 5, Table 2) prepared by catalyst-switch strategy (TCB, 150 °C, PS standards).

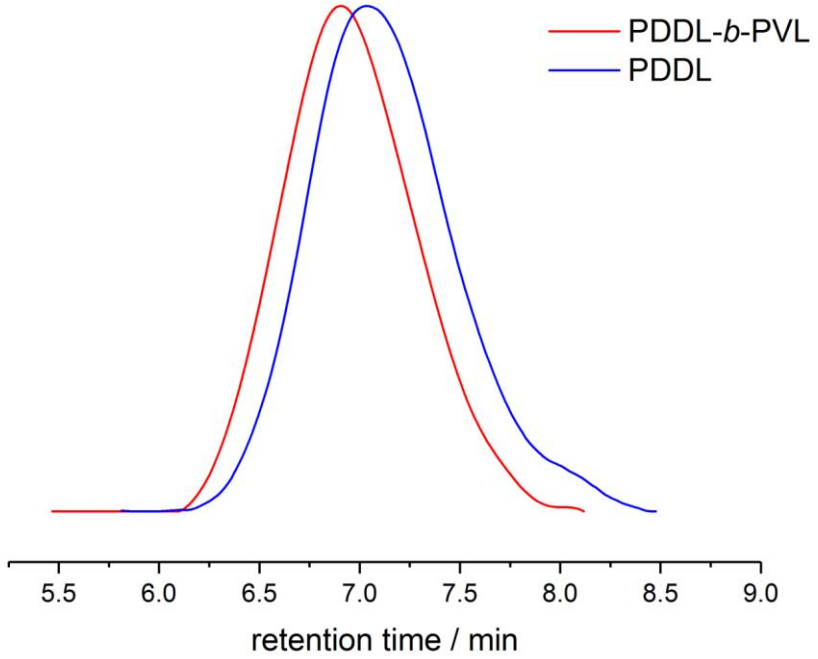


Figure S23. HT-GPC traces of PDDL (blue) macroinitiator and PDDL-*b*-PVL (red, entry 6, Table 2) prepared by catalyst-switch strategy (TCB, 150 °C, PS standards).

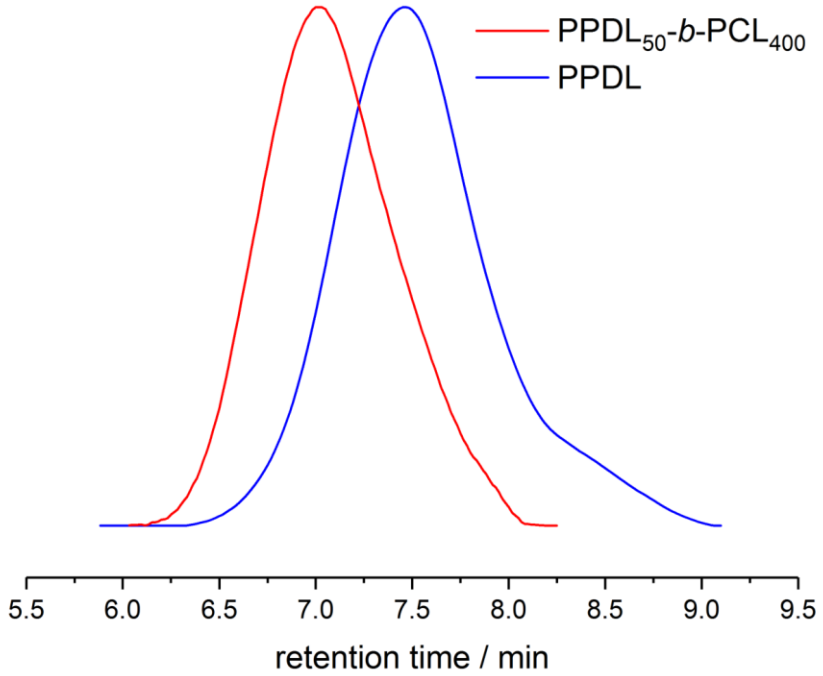


Figure S24. HT-GPC traces of PPDL (blue) macroinitiator and $PPDL_{50}$-*b*-PCL_{400} (red, entry 7, Table 2) prepared by catalyst-switch strategy (TCB, 150 °C, PS standards).

Table S1. Properties of PMLs:PSLs blends

entry	sample	mass (mg)		PSL (°C)		PML (°C)		ΔH_m[a] (J g^{-1})	
		PSL	PML	T_c[a]	T_m[a]	T_c[a]	T_m[a]	PSL	PML
1	PPDL:PCL	1.2	2.8	38.5	53.7	79.6	92.6	–23.8	–78.6
2	PPDL:PVL	1.0	3.0	39.5	57.2	78.9	92.7	–20.3	–80.4
3	PHDL:PCL	1.0	3.0	43.9	55.7	76.2	91.6	–16.8	–86.2
4	PHDL:PVL	0.8	3.2	44.7	58.0	76.3	90.8	–12.9	–89.6
5	PDDL:PCL	1.4	2.6	36.5	53.6	67.7	83.4	–28.8	–65.9
6	PDDL:PVL	0.8	3.2	38.3	55.6	67.0	83.3	–16.5	–79.8
7	$PPDL_{50}$:PCL_{400}	3.2	0.8	37.2	53.8	80.5	93.0	–68.4	–17.3

[a]Measured by DSC under air with heating rate 10 °C min^{-1}.

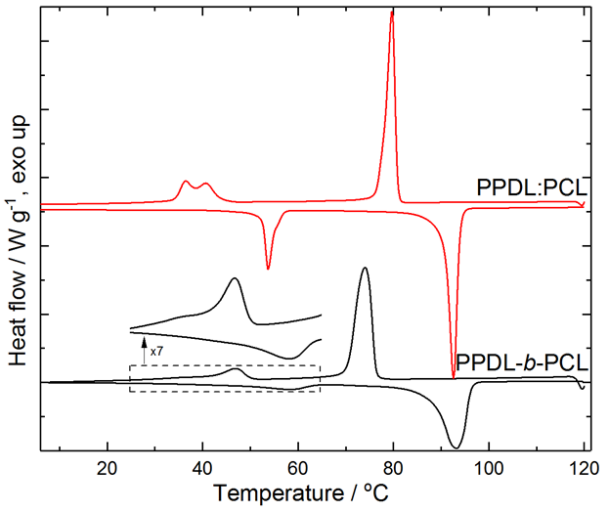


Figure S25. DSC traces of PPDL-*b*-PCL (black, entry 1, Table 2) prepared by catalyst-switch strategy and PPDL: PCL blend (red) (under air, 10 °C min^{-1}).

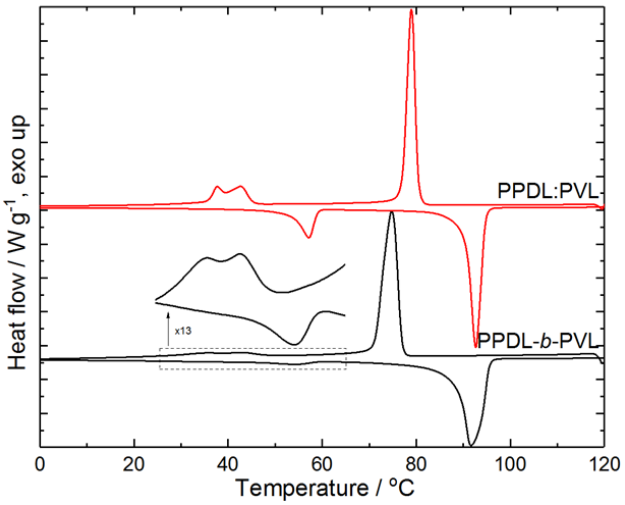


Figure S26. DSC traces of PPDL-*b*-PVL (black, entry 2, Table 2) prepared by catalyst-switch strategy and PPDL: PVL blend (red) (under air, 10 ˚C min^{-1}).

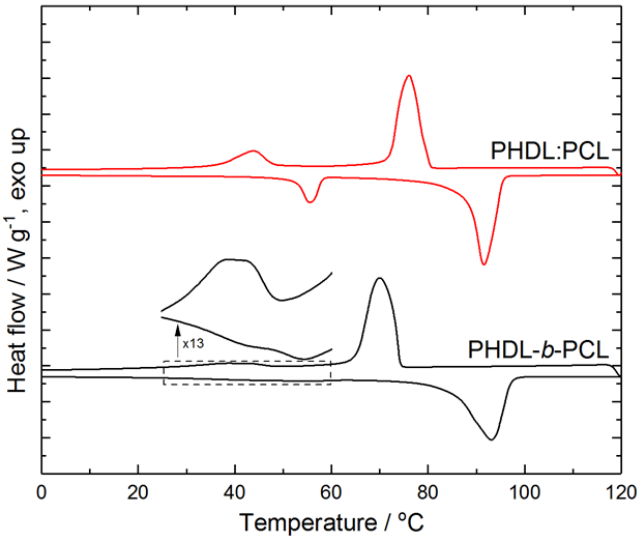


Figure S27. DSC traces of PHDL-*b*-PCL (black, entry 3, Table 2) prepared by catalyst-switch strategy and PHDL: PCL blend (red) (under air, 10 ˚C min^{-1}).

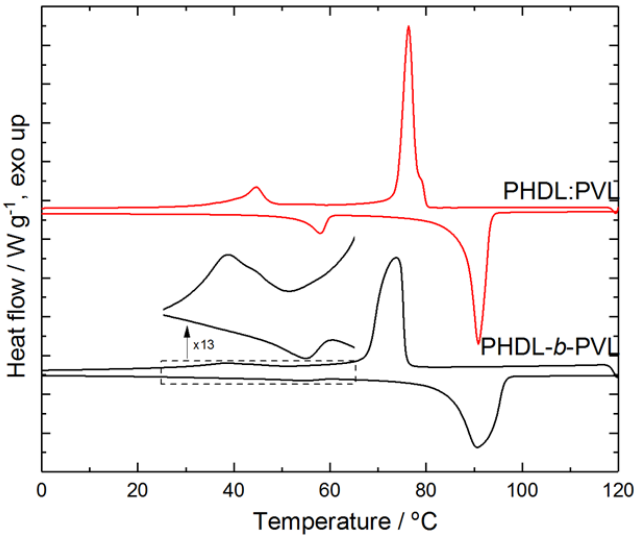


Figure S28. DSC traces of PHDL-*b*-PVL (black, entry 4, Table 2) prepared by catalyst-switch strategy and PHDL: PVL blend (red) (under air, 10 ˚C min^{-1}).

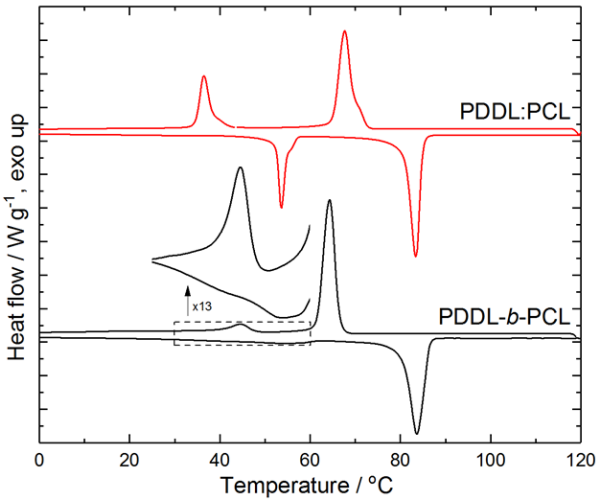


Figure S29. DSC traces of PDDL-*b*-PCL (black, entry 5, Table 2) prepared by catalyst-switch strategy and PDDL: PCL blend (red) (under air, 10 ˚C min^{-1}).

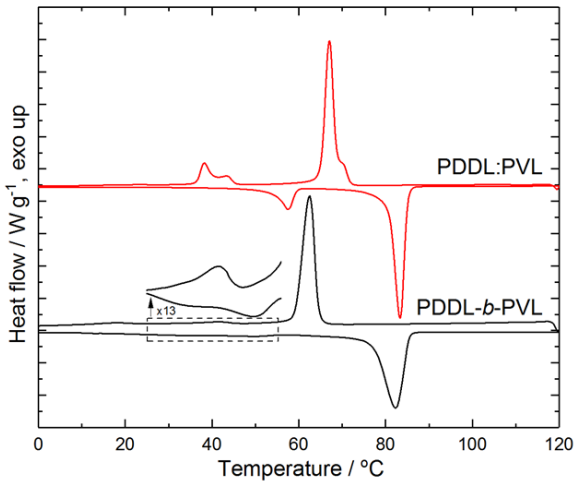


Figure S30. DSC traces of PDDL-*b*-PVL (black, entry 6, Table 2) prepared by catalyst-switch strategy and PDDL: PVL blend (red) (under air, 10 ˚C min^{-1}).

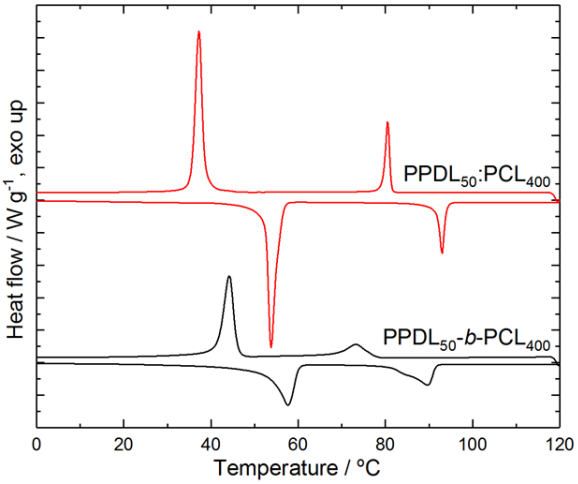


Figure S31. DSC traces of $PPDL_{50}$-*b*-PCL_{400} (black, entry 7, Table 2) prepared by catalyst-switch strategy and $PPDL_{50}$:PCL_{400} blend (red) (under air, 10 ˚C min^{-1}).

Table S2. Peaks position of PMLs and PSLs in XRD spectra

run	sample	Peak 1[a] (2θ)	Peak 2 [a] ($2\ \theta$)
1	PPDL-*b*-PCL	21.6	24.0
2	PPDL-*b*-PVL	21.6	24.0
3	PHDL-*b*-PCL	21.5	23.9
4	PHDL-*b*-PVL	21.6	24.0
5	PDDL-*b*-PCL	21.5	24.0
6	PDDL-*b*-PVL	21.6	24.0
7	$PPDL_{30}$-*b*-PCL_{200}	21.5	23.8
8	PCL	21.5	23.7
		22.1	
9	PVL	21.7	24.4
10	PPDL	21.6	24.0
11	PHDL	21.5	23.9
12	PDDL	21.5	23.9

[a]Determined by XRD under ambient condition.